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(54) CORROSION RESISTANT MEMBER

(57)Abstract:
PROBLEM TO BE SOLVED: To prevent the falling of grains from the surface of a sintered compact of glass, stainless steel, alumina or AlN used so far and the generation of particles by gradual progress of corrosion caused owing to unsatisfactory corrosion resistance to fluorine-contg. plasma.
SOLUTION: A part of a member exposed to fluorine-contg. corrosive gas such as CF4 or SF4 or plasma of the gas is made of a sintered compact of a multiple oxide contg. a group IIIa metal of the Periodic Table such as Y, La, Ce, Nd or Dy and Al and/or Si, e.g. 3Y2O3.5Al2O3, 2Y2O3.Al2O3, Y2O3.Al2O3, a di- or monosilicate.

CLAIMS

[Claim(s)]
[Claim 1] The corrosion-resistant member characterized by the part put to fluorine system corrosion gas or its plasma consisting of a periodic table 3a group metal and a multiple oxide containing aluminum and/or Si.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the corrosion-resistant member used

as discharge walls, such as lamps, such as the discharge tubes, such as wall material of the plasma treatment equipment which has high corrosion resistance to fluorine system corrosive gas and the fluorine system plasma especially, or the objects for semi-conductor manufacture or the plasma process units for liquid crystal, and a fixture, and metal halide.

[0002]

[Description of the Prior Art] Utilization of plasma, such as a dry process of semi-conductor manufacture, plasma jet flame coating, the discharge tube, and a lamp, is progressing quickly in recent years. As a plasma process in a semi-conductor, halogen system corrosion gas, such as a fluorine system, is used for vapor growth, etching, or cleaning from the reactant height.

[0003] Corrosion-resistant metals, such as an ingredient with which the member which high corrosion resistance is required of the member in contact with these corrosive gas, and contacts these plasma other than a processed material conventionally generally uses SiO(s)2, such as glass and a quartz, as a principal component, and stainless steel, Monel, are used abundantly.

[0004] Moreover, it is used noting that what carried out surface coating of an alumina sintered compact, sapphire, the sintered compact of AlN, or these with the CVD method etc. by making a wafer into the susceptor material which carries out support immobilization at the time of semi-conductor manufacture manufacture is excellent in corrosion resistance. Moreover, the heater which coated graphite and boron nitride is used.

[0005]

[Problem(s) to be Solved by the Invention] however, if glass and the quartz of the corrosion resistance in the plasma which are used from the former are inadequate, and consumption is intense and touches especially the fluorine plasma, the contact surface will etch -- having -- a front face -- description changed, and in the member for which light transmission nature is needed, a front face is white gradually and the problem of translucency falling had produced the overcast.

[0006] Moreover, since the corrosion resistance of the member which used metals, such as stainless steel, was inadequate, especially in semi-conductor manufacture, it had become the cause of defective generating by corrosion.

[0007] Although an alumina and the sintered compact of AlN are excellent in corrosion resistance to fluorine system gas as compared with the above-mentioned ingredient, when the plasma was touched at the elevated temperature, corrosion advanced gradually, degraining of a crystal grain child arose from the front face of a sintered compact, and the problem of becoming the cause of particle generating has occurred.

[0008]

[Means for Solving the Problem] As a result of this invention persons' repeating examination about the approach for raising the corrosion resistance over fluorine system corrosion gas and the plasma, if a reaction with fluorine system corrosion gas or the plasma advances, a high-melting fluoride will be generated first, especially -- the [periodic table] -- the multiple oxide with 3a group element, aluminum, and/or Si while being able to obtain cheaply, the fluoride forms a stable fluoride layer in a front face, and corrosive [of a member] controls -- having -- the conventional alumina, glass, AlN, and Si3 N4 etc. -- the knowledge of the outstanding corrosion resistance being realizable is carried out.

[0009] namely, the part in the corrosion-resistant member which the corrosion-resistant member of this invention is completed based on the above-mentioned

knowledge, and is put to fluorine system corrosion gas or its plasma which contacts said corrosion gas and plasma directly at least -- the [periodic-table] -- the comparatively cheap member which has the resistance of long duration in an elevated temperature and the fluorine system corrosion ambient atmosphere of high density can be offered by constituting with 3a group element and the multiple oxide containing aluminum and/or Si.

[0010] as the member which is put to fluorine system gas and the plasma according to this invention -- the [periodic table] -- by using 3a group element and the multiple oxide ingredient containing aluminum and/or Si, a material-list side generates a stable fluoride layer by the reaction with a fluorine, and the improvement in resistance to a severe fluorine system corrosion ambient atmosphere is attained in a broad temperature requirement. Furthermore, by suppressing the deposit to the grain boundary of element compounds, such as Si, germanium, Mo, etc. which react with a fluorine and volatilize easily, and preventing the omnipresence, degraining and particle generating which considered corrosion resistance local lowering and local it as the cause are prevented, and it becomes possible to aim at further corrosion resistance improvement. although these elements volatilize by the initial stage of corrosion -- a material-list side -- the -- a fluoride including 3a group -- remaining -- gradually -- the -- progress of corrosion can be controlled as a result of forming the fluoride layer which is rich in 3a group element.

[0011] the [and / periodic table] -- 3a group element and the multiple oxide containing aluminum and/or Si -- the [periodic table] -- since it cannot stop at forming by thin film technologies, such as PVD and a CVD method, as compared with 3a group element oxide but can produce as a precise sintered compact, it becomes possible to suit all configuration articles.

[0012]

[Embodiment of the Invention] The corrosion-resistant member of this invention is a member put to the corrosion gas or the fluorine system plasma of a fluorine system, and as fluorine system gas, SF6, CF4, CHF3, ClF3, HF, etc. are mentioned, and if microwave, a RF, etc. are introduced into the ambient atmosphere into which these gas was introduced, these gas will be plasma-ized.

[0013] the part which is put to such fluorine system gas or its plasma according to this invention -- at least -- the [periodic table] -- it constitutes from a multiple oxide containing 3a group element, and aluminum and/or Si. the [which constitutes a multiple oxide here / periodic table] -- as 3a group element -- any, such as Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu, -- although used, Y, La, Ce, Nd, and Dy are especially desirable in respect of cost.

[0014] the corrosion resistance of this multiple oxide -- the [periodic table] -- the amount of 3a group elements is influenced greatly -- having -- the [periodic table] -- as for especially 3a group element, existing more than 40 atom % is desirable more than 30 atom % among all the metallic elements in a multiple oxide. this -- the [periodic table] -- if there are few amounts of 3a group elements than 30 atom %, although the corrosion in early stages of the inside of halogenation gas or its plasma will be intense and a protective layer will be gradually formed in a front face, it is not practical in order to require long duration.

[0015] Moreover, although you may be a single crystal besides the glass containing at least two sorts of above-mentioned metallic elements, and a ceramic sintered compact as a multiple oxide, when the corrosion resistance of the grain boundary phase which deposited in the grain boundary is more remarkably [than the main crystal grain child] inferior in the case of a ceramic sintered compact, it is corroded selectively and

a grain boundary phase causes degraining and particle generating. Therefore, as for the content in the grain boundary of Si, germanium, Mo, and W which tend to be corroded by the fluorine, it is desirable to stop to 1 or less % of the weight among the whole quantity. It is not this limitation, when the element which tends to be corroded by these fluorines dissolves in the main crystal grain child and does not exist in a grain boundary.

[0016] A multiple oxide is good desirably to make a crystalline substance into a subject. Especially Garnet mold crystals, such as YAG (3Y2 O3 and 5aluminum 2O3), Perovskite mold crystals, such as monoclinic system mold crystals, such as YAM (2Y2 O3 and aluminum 2O3), and YAP (Y2 O3 and aluminum 2O3), It is desirable at the point of having the corrosion resistance excellent in what makes a subject silicate compounds, such as mono-silicate (Y2 O3 and SiO2) and die silicate (Y2O3 and 2SiO2). A garnet mold crystal and a die silicate mold crystal have a degree of sintering and the most desirable manufacturing cost also in these at a cheap point.

[0017] moreover, the sintered compact of the above-mentioned multiple oxide -- the [for example, / periodic table] -- 3a group element oxide and aluminum 2O3 Or SiO2 It is producible by calcinating mixture with powder in [of 1100-1900 degrees C] an oxidizing atmosphere or a vacuum ambient atmosphere. As the baking approach, hot pressing besides ordinary pressure baking etc. is adopted.

[0018] Moreover, as a corrosion-resistant member of this invention, it may not remain in this sintered compact, but you may form in a predetermined base front face as a thin film by the well-known thin film forming methods, such as PVD and a CVD method. Moreover, the thin film which applied the liquid phase with the well-known sol gel process, and was calcinated is sufficient. Although this multiple oxide is formed in addition in the most desirable part put to halogen system corrosion gas or its plasma in these from it being excellent in the applicability to all members that it is the sintered compact which fabricated and calcinated powder, this metallic oxide is desirable when it gives the outstanding corrosion resistance that that thickness is 10 micrometers or more at least. That is, it is because the anticorrosion effectiveness which was excellent when the thickness was thinner than 10 micrometers is not expectable.

[0019]

[Example] Various kinds of ingredients of a publication were produced to a table 1 - a table 3 using various oxide powder. The inside of a table 1 and sample No.1-5 are the rare earth oxide of a table 1, and SiO2. And/or, aluminum 2O3 It quenches and vitrifies, after fusing mixture at 2000 degrees C. Seven are sample No.6 andY2O3. SiO2 The Plastic solid mixed at a predetermined rate is calcinated at 1300-1600 degrees C. Sample No.8-13 are Y2 O3. aluminum 2O3 The Plastic solid which consists of mixture is calcinated in a 1600-1900-degree C oxidizing quality or a vacuum ambient atmosphere. sample No. -- 14 and 15 -- the rare earth oxide and aluminum 2O3 of a table 1 The Plastic solid which consists of mixture is calcinated at 1400-1750 degrees C. sample No. -- 16 and 17 -- Sc 2O3 aluminum 2O3 It considers as a target and produces by the spatter. In addition, eburnation of each sintered compact was carried out to 95% or more of relative density.

[0020] And the various ingredients of a table 1 are installed in a RIE plasma etching system, and it is CF4. O2 Mixed gas (CF4:O2 =9:1), and Ar and SF6 While introducing either of mixed gas (Ar:SF 6 = 2:3), microwave was introduced and the plasma was generated. It held in this plasma for a maximum of 3 hours, weight reduction of the ingredient before and behind processing was measured, and the ' thickness (etch rate) into which per minute is etched from that value was computed.

Moreover, the surface state of the sample after a trial was observed and the result was shown in a table 1.
[0021] In addition, the conventional BN sintered compact as an example of a comparison, quartz glass, and Si3 N4 A sintered compact and aluminum 2O3 It examined similarly about the sintered compact and the AlN sintered compact.
[0022]
[A table 1]

[0023] As shown in a table 1, an etch rate exceeds 50A / min, moreover as for each various conventional ingredient, the dry area of a surface state is severe, and it is Si3 N4. In the sintered compact, generating of particle was checked on the front face. aluminum 2O3 Many hollows also according [the sintered compact of AlN] to etching were observed.
[0024] The sample of this invention of sample No.1-17 all showed high corrosion resistance to the fluorine system plasma to these examples of a comparison. Each thing which especially the thing which a sample gestalt becomes from glass turns into from a sintered compact or a thin film although formation of a hollow was checked on the front face was excellent also in the surface state. after [moreover,] examining in any sample of this invention -- <TXF FR=0002 HE=055 WI=080 LX=1100 LY=1600> -- it is -- the [periodic table] -- it checked that the fluoride layer which is rich in 3a group element was formed in a front face.
[0025]
[Effect of the Invention] as the member which is put to fluorine system corrosive gas and its plasma according to this invention as explained in full detail above -- the [periodic table] -- with constituting with the multiple oxide of 3a group element, and aluminum and/or Si, a material-list side generates a stable fluoride layer at least, and high corrosion resistance is attained by the severe fluorine system corrosion ambient atmosphere. And since a sintered compact is easily producible, it is applicable to all configuration articles.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the corrosion-resistant member used as discharge walls, such as lamps, such as the discharge tubes, such as wall material of the plasma treatment equipment which has high corrosion resistance to fluorine system corrosive gas and the fluorine system plasma especially, or the objects for semi-conductor manufacture or the plasma process units for liquid crystal, and a fixture, and metal halide.

PRIOR ART

[Description of the Prior Art] Utilization of plasma, such as a dry process of semi-conductor manufacture, plasma jet flame coating, the discharge tube, and a lamp, is progressing quickly in recent years. As a plasma process in a semi-conductor, halogen system corrosion gas, such as a fluorine system, is used for vapor growth, etching, or cleaning from the reactant height.
[0003] Corrosion-resistant metals, such as an ingredient with which the member

which high corrosion resistance is required of the member in contact with these corrosive gas, and contacts these plasma other than a processed material conventionally generally uses SiO(s)2, such as glass and a quartz, as a principal component, and stainless steel, Monel, are used abundantly.
[0004] Moreover, it is used noting that what carried out surface coating of an alumina sintered compact, sapphire, the sintered compact of AlN, or these with the CVD method etc. by making a wafer into the susceptor material which carries out support immobilization at the time of semi-conductor manufacture manufacture is excellent in corrosion resistance. Moreover, the heater which coated graphite and boron nitride is used.

EFFECT OF THE INVENTION

[Effect of the Invention] as the member which is put to fluorine system corrosive gas and its plasma according to this invention as explained in full detail above -- the [periodic table] -- with constituting with the multiple oxide of 3a group element, and aluminum and/or Si, a material-list side generates a stable fluoride layer at least, and high corrosion resistance is attained by the severe fluorine system corrosion ambient atmosphere. And since a sintered compact is easily producible, it is applicable to all configuration articles.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] however, if glass and the quartz of the corrosion resistance in the plasma which are used from the former are inadequate, and consumption is intense and touches especially the fluorine plasma, the contact surface will etch -- having -- a front face -- description changed, and in the member for which light transmission nature is needed, a front face is white gradually and the problem of translucency falling had produced the overcast.
[0006] Moreover, since the corrosion resistance of the member which used metals, such as stainless steel, was inadequate, especially in semi-conductor manufacture, it had become the cause of defective generating by corrosion.
[0007] Although an alumina and the sintered compact of AlN are excellent in corrosion resistance to fluorine system gas as compared with the above-mentioned ingredient, when the plasma was touched at the elevated temperature, corrosion advanced gradually, degraining of a crystal grain child arose from the front face of a sintered compact, and the problem of becoming the cause of particle generating has occurred.

MEANS

[Means for Solving the Problem] As a result of this invention persons' repeating examination about the approach for raising the corrosion resistance over fluorine system corrosion gas and the plasma, if a reaction with fluorine system corrosion gas or the plasma advances, a high-melting fluoride will be generated first, especially -- the [periodic table] -- the multiple oxide with 3a group element, aluminum, and/or Si while being able to obtain cheaply, the fluoride forms a stable fluoride layer in a front

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